

Distribution of Diffusion Constants and Stokes-Einstein Violation in supercooled liquids

Shiladitya Sengupta^{1,2} and Smarajit Karmakar²

¹*Theoretical Sciences Unit, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur Campus, Bangalore 560 064, India.*

²*TIFR Centre for Interdisciplinary Sciences, 21 Brundavan Colony, Narsingi, Hyderabad 500075, India.*

It is widely believed that the breakdown of the Stokes-Einstein relation between the translational diffusivity and the shear viscosity in supercooled liquids is due to the development of dynamic heterogeneity *i.e.* the presence of both slow and fast moving particles in the system. In this study we *directly* calculate the distribution of the diffusion constant for a model system for different temperatures in the supercooled regime. We find that with decreasing temperature, the distribution evolves from Gaussian to bimodal indicating that on the time scale of the α relaxation time, mobile (liquid like) and less mobile (solid like) particles in the system can be *unambiguously* identified. We also show that less mobile particles obey the Stokes-Einstein relation even in the supercooled regime and it is the mobile particles which show strong violation of the Stokes-Einstein relation. Finally, we show that the degree of violation of the Stokes-Einstein relation can be tuned by introducing randomly pinned particles in the system.

INTRODUCTION

In normal liquids, the shear viscosity (η) is related to the translational diffusion constant (D) of a particle diffusing through it *via* the Stokes-Einstein (SE) relation [1–3] as $D = \frac{cT}{\eta}$, where c is a constant which depends on the details of the particle and boundary conditions and T is the temperature. Although, originally derived for a macroscopic probe particle in the hydrodynamic limit, the SE relation also holds for the *self* diffusion of liquid particles at high temperatures [4]. However, it has been shown extensively [5–20] that when a liquid is supercooled the SE relation breaks down *i.e.* the measured self diffusivity becomes much larger than the value predicted by the SE relation. Often the shear viscosity is substituted by the relaxation time (τ) which is cheaper to compute and more commonly treated in theories.

Phenomenological arguments *e.g.* by Stillinger and Hodgdon [4] and by Tarjus and Kivelson [11] have shown that by considering supercooled liquids to consist of mobile “fluid-like” and less mobile “solid-like” regions, the decoupling between the translational diffusion (D) and the relaxation time (τ) is explained naturally because the average diffusion constant is predominantly determined by the “fluid like” regions whereas the average relaxation time is dominated by the “solid-like” regions. The existence of clusters (with finite lifetime) of mobile and less mobile particles has been directly shown in many different studies [21–23] and is known as the dynamical heterogeneity (DH). However, the above-mentioned phenomenological theory of decoupling is based on the existence of a distribution of diffusivity (relaxation times) whereas previous studies on DH have typically analyzed the distribution of particle displacements. Hence not much direct information about the existence and nature of the diffusivity (relaxation time) distribution is available.

There are however, *indirect* evidences, *e.g.* the universal exponential tail in the Van Hove functions [24] seen for many supercooled liquids, which supports the existence of a distribution of diffusivity (relaxation times). Consider an extreme case where the system has regions with two diffusivity - one for “solid like” (D_s) and the other for “liquid like” regions (D_l). Hence a distribution of diffusivity can be written as $p(D) = A\delta(D_s) + B\delta(D_l)$ where A and B are fixed by the normalization condition and the amount of solid like and liquid like regions. Now if we calculate the van Hove correlation function as

$$G_s(x, t) = \int dD p(D) g(x|D), \quad (1)$$

where $g(x|D) = \frac{1}{\sqrt{4\pi Dt}} \exp\left(-\frac{x^2}{4Dt}\right)$ then one may show that the van Hove function will have a long tail and depending on the distribution of the $p(D)$, the tail of the distribution can be either exponential or Gaussian [25]. In general the exponential tail has been reported [24] which, as mentioned in [25], might be due to the small range of the data.

The main aim of this study is to calculate *directly* the distribution of the diffusivity from the simulation data. From the previous discussion, one may expect that in deeply supercooled liquids the distribution of diffusivity ($p(D)$) will be bimodal in general. Unlike previous works [26–28] where the presence of two types of particles with distinct mobilities are inferred indirectly from the distribution of displacements, our method directly and unambiguously shows that the distribution of the diffusivity becomes bimodal below some temperature. Note that the bimodal nature of the distribution only says that there are two types of particles in the system, but it does not prove that these particles are clustered together to form “solid like” and “fluid-like” regions. Hence bimodal distributions of diffusivity alone is not enough to justify the picture of supercooled liquids being a sparse mixture of

“fluid like” and “solid like” regions. Using random pinning geometry we further show that indeed one has “fluid like” and “solid like” regions in the system up to some time scale of the order of α relaxation time, τ_α .

We end this section by noting that the phenomenological explanation of decoupling does not tell anything about the nature and origin of the heterogeneity. Microscopic theories to understand decoupling from the dynamic heterogeneity *e.g.* mode coupling theory (MCT) [29], random first-order transition (RFOT) theory [30–32], shear transformation zone (STZ) theory [33], dynamical facilitation [34] and the obstruction model [35] do not mutually agree on the origin and the nature of heterogeneous dynamics. Besides, the decoupling of D and τ may also be explained in terms of a growing length scale [27, 36] which does not directly require a distribution of diffusivity (relaxation times).

DISTRIBUTION OF DIFFUSIVITY

Below we explain briefly the method used to extract the distribution of diffusivity directly from the van Hove correlation function $G_s(x, \tau)$ using the iterative algorithm suggested in [37] and recently used in [25] for the diffusion processes in biological systems. We start with the definition of van Hove correlation function

$$G_s(x, \tau) = \langle \delta [x - (x_i(\tau) - x_i(0))] \rangle, \quad (2)$$

where the $\langle . \rangle$ implies averaging over the time origin. Now if we assume that particle displacements are caused by diffusion processes and there is a distribution of local diffusivity $p(D)$, then we can express $G_s(x, \tau)$ in terms of $p(D)$ as

$$G_s(x, \tau) = \int_0^{D_0} p(D) \cdot g(x|D) \cdot dD, \quad (3)$$

where $g(x|D) = 1/\sqrt{4\pi D\tau} \exp(-x^2/4D\tau)$ and D_0 is the upper limit of diffusion constant and will be equal to diffusivity for a free diffusion. Now given the $G_s(x, \tau)$ we calculate the distribution of diffusivity $p(D)$ following [37] as

$$p^{n+1}(D) = p^n(D) \int_{-\infty}^{\infty} \frac{G_s(x, \tau)}{G_s^n(x, \tau)} g(x|D) dx, \quad (4)$$

where $p^n(D)$ is the estimate of $p(D)$ in the n^{th} iteration with $p^0(D) = (1/D_{avg}) \exp(-D/D_{avg})$ and

$$G_s^n(x, \tau) = \int_0^{D_0} p^n(D) \cdot g(x|D) \cdot dD. \quad (5)$$

Similarly

$$P^{n+1}(D\tau) = P^n(D\tau) \int_{-\infty}^{\infty} \frac{G_s(x, \tau)}{G_s^n(x, \tau)} g(x|D) dx, \quad (6)$$

where $p(D)dD = P(D\tau)d(D\tau)$. The choice of $D\tau$ as our variable is due to the fact that D changes by several orders of magnitude in the studied temperature range whereas $D\tau$ changes relatively modestly with decreasing temperature and it will be easier to compare the distribution obtained for different temperatures.

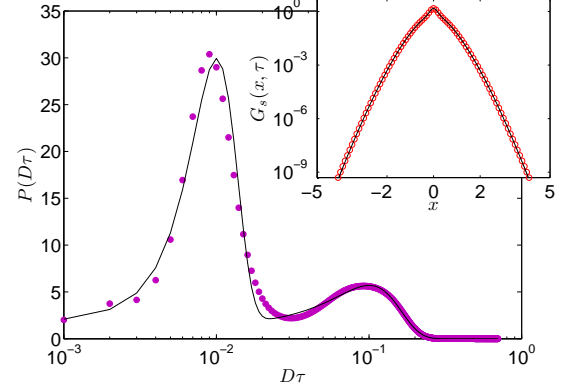


FIG. 1: The solid line shows the results of the iterative scheme used to calculate the distribution of diffusivity (see text for details) along with the original distribution shown as symbols. The agreement is really encouraging and inset shows the corresponding comparison for the van Hove correlation functions.

We tested on a toy model whether the above mentioned iterative scheme converges to the correct solution. We started with a distribution $P(D\tau)$ and calculated the van Hove correlation function $G_s(x, \tau)$ using Eq.3, and then used this to recalculate the probability distribution $P(D\tau)$ using Eq.6. In Fig.1, we have compared the obtained distribution $P(D\tau)$ with the input distribution. The agreement is really amazing with moderate number of iterations. In the inset we have compared the van Hove function obtained from the converged distribution of diffusivity with the exact one. Here also the agreement is near perfect. Note that the iterative scheme does not depend at all on the initial guess distribution.

After establishing the rapid convergence of the iterative scheme to the correct solution we tried to calculate the distribution of diffusivity for a model glass forming liquid, the Kob-Andersen Model [38]. To compare the van Hove functions for different temperatures we calculated it for the time τ_m when the mean square displacement becomes half the inter particle diameter i.e. $\langle \Delta r^2(\tau_m) \rangle = 0.50$ as shown in Fig.2. The temperature dependence of τ_m is very different from the α -relaxation time τ_α calculated from the normalized two point correlation function as $\langle Q(\tau_\alpha) \rangle = 1/e$. In the inset of Fig.2, we have shown τ_m and τ_α as a function of temperature. This is another manifestation of the Stokes-Einstein (SE) violation in this model.

To extract the distribution function of the diffusivity one needs to supply somewhat smoothly averaged data of

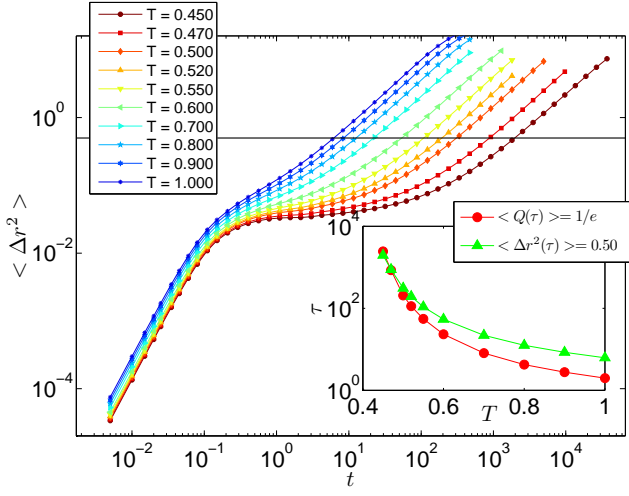


FIG. 2: Mean Squared displacement (MSD) for different temperature and the horizontal line indicates the time where mean squared displacement reaches 0.50 in the units of particle diameter for different temperature. The corresponding time is denoted as τ_m here (see text for details). Inset: Comparison of the α -relaxation time τ_α calculated from the normalized two point correlation function as $\langle Q(\tau_\alpha) \rangle = 1/e$ with τ_m .

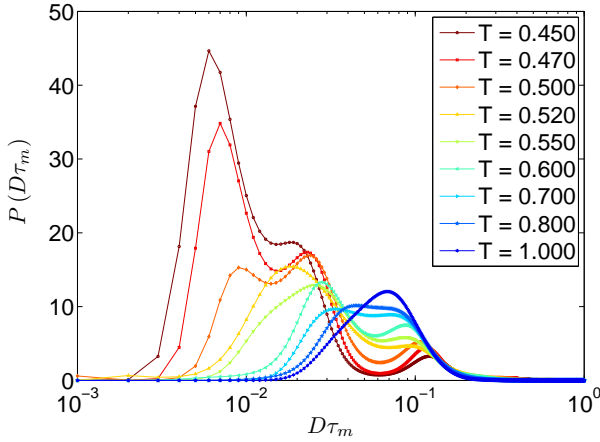


FIG. 3: Calculated distribution of the diffusivity for different temperatures. Notice the appearance of the bimodality in the distribution just below the onset temperature $T = 1.00$. Clear bimodal distribution in the supercooled regime confirms that there are two different types of particles in terms of their mobility up to time scale of typical relaxation time. The appearance of more peaks in the distribution at still further lower temperature is really interesting, indicating possibility of extremely slow to moderately slow to very fast particles in very deep supercooled state.

the van Hove correlation function $G_s(x, \tau_m)$ for the iterative scheme to converge fast. In this study we fitted the extreme tail of the calculated $G_s(x, \tau_m)$ using exponential function as this part is in general noisy and difficult to average. In Fig.3, we have shown the distributions of

the diffusivity $P(D\tau_m)$ as function of temperature and in Fig.4, we showed the van Hove correlation functions calculated from these distributions of diffusivity along with the simulation data. The agreement between the simulation data and the calculated ones is fantastic. An important point to mention here is that tails of these van Hove correlation functions can not be completely described by a single exponential function over the whole range at least for the low temperature data ($T \leq 0.50$). Rather they can be better fitted by two exponential functions.

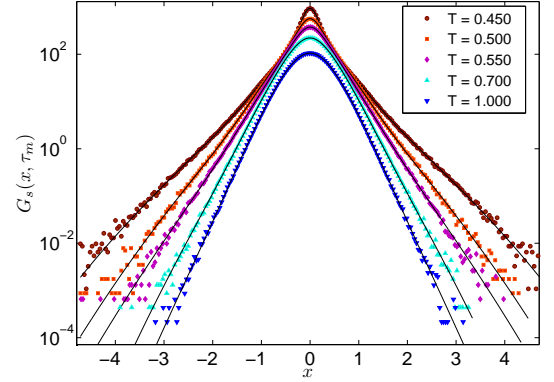


FIG. 4: The van Hove correlation functions (solid line) as obtained from the iterative scheme (see text for details) along with the simulation data (symbols). The curves are shifted upward for clarity and to point out that the line goes through the data points over the whole range of the data.

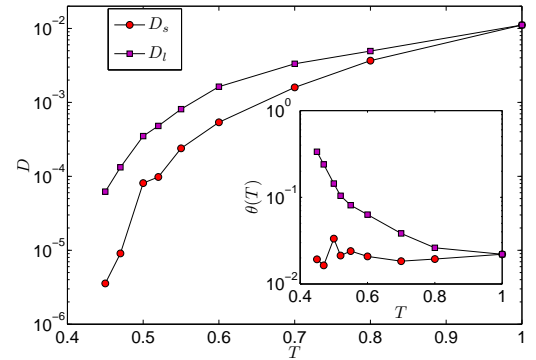


FIG. 5: The temperature dependence of the diffusivity associated with the solid like (D_s) and liquid like (D_l) particles. These values are calculated from the peak positions of the distributions in Fig.3. Inset : The Stokes-Einstein violation parameter $\theta(T) = \frac{D\tau_\alpha}{T}$ for the two types of particles. One sees clearly that solid like particles obey Stokes-Einstein relation to a reasonable accuracy over the whole temperature range and it is the liquid like particles which show strong Stokes-Einstein violation.

Now looking at Fig.3, we can see that just below the onset temperature ($T = 1.00$), the distribution starts to become bimodal and two peaks clearly emerge at temper-

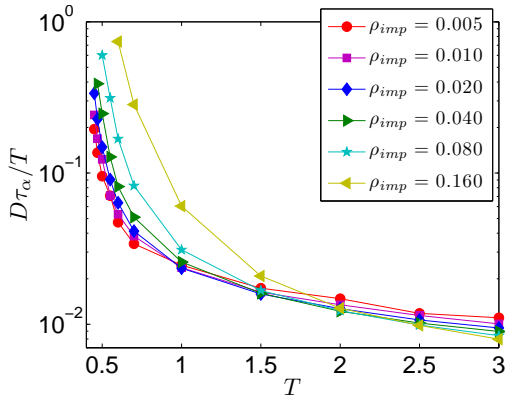


FIG. 6: Stokes-Einstein violation parameter has been shown as a function of temperature for different density of the frozen particles ρ_{imp} . One can clearly see that the deviation from the Stokes-Einstein relation becomes stronger with increasing density of the frozen particles.

ature around $T = 0.60$. At further lower temperatures the distribution seems to show existence of shoulder or another peak but the peak at large diffusivity remains intact although with decreasing peak height. Thus we have clearly demonstrated that there are two types of particles in the supercooled liquid. One is more solid like (less mobile) than the other in the time scale of the order of α relaxation time, τ_α . It is worth noticing that the width of the distribution increases with decreasing temperature which indicates increase of DH leading to stronger SE breakdown[17].

In the top panel of Fig.5, we have shown the temperature dependence of the diffusivity associated with the solid like (D_s) and the liquid like (D_l) particles. Here we took the peak position as an estimator for the diffusion constants for solid and liquid like particles. At the lowest three temperatures shoulders seem to appear in the distributions, but we calculated the peak position to be the position of the dominant peak. In the lower panel of Fig.5, we calculated the Stokes-Einstein violation parameter $\theta(T) = \frac{D\tau_\alpha}{T}$ for the two set of particles. One clearly sees that solid like particles obey the Stokes-Einstein relation over the whole temperature range, whereas the liquid like particles show strong SE violation leading to overall violation of the SE relation in the liquid. A similar conclusion is reached in [26].

After establishing the fact that two types of particles can be identified in the system on a time scale of α relaxation time, we now turn to the question of whether the “solid-like” particles group together to form clusters. To answer this question we performed another set of simulation experiments where we randomly freeze (random pinning geometry) some of the particles and then ask what is the effect of this on the dynamics of the system. If the “solid like” particles are clustered together to form a region then if we randomly freeze some of the parti-

cles in the system, there will always be instances where these frozen particles are part of these “solid like” regions. In that case, due to the frozen particles the relaxation of these regions will be hindered further and the relaxation time of the whole system will increase dramatically with increasing density of these frozen particles. However, these frozen particles will have very small effect on diffusivity which is mainly governed by the “fluid like” particles, so the diffusivity will not change that dramatically. In this scenario one expects to see an enhancement of the Stokes-Einstein breakdown if one increases the number density ρ_{imp} of the randomly frozen particles. On the contrary if the clusters of “solid-like” particles are not present in the system then we expect that changing the density of randomly frozen particles will have little effect on the relaxation dynamics of these regions *i.e.* no dependence of the SE violation parameter with ρ_{imp} . In Fig.6, we have shown the temperature dependence of the Stokes-Einstein violation parameter $\theta(T) = \frac{D\tau_\alpha}{T}$ for different pinning densities ρ_{imp} . The deviation of $\theta(T)$ from being a constant as a function of temperature with increasing ρ_{imp} is very dramatic.

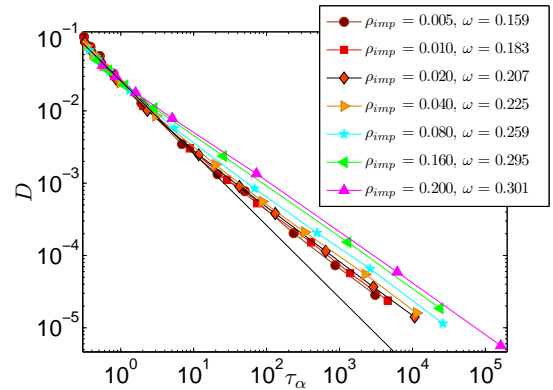


FIG. 7: Diffusivity (D) plotted as a function of relaxation time (τ_α) for different density of the frozen particles ρ_{imp} in log-log to show the power law relationship between these quantities expected from the fractional Stokes-Einstein Relation $D \propto \tau_\alpha^{-1+\omega}$, with $\omega \geq 0$. Notice that the exponent ω increase with increasing pinning density ρ_{imp} indicating a stronger breakdown of the Stokes-Einstein Relation. The solid line has a slope equal to -1.0.

In literature people often use a fractional Stokes-Einstein relation [9, 14, 35] to fit the data where the original relation breaks down. We tried similar fits to the low temperature data using the form $D \propto \tau_\alpha^{-1+\omega}$, with $\omega \geq 0$. In Fig.7, we have shown that our data can be well represented by the fractional Stokes-Einstein relation in the low temperature range with ω increasing with increasing ρ_{imp} . Now it is important to mention that in the past many people have tried to tune the Stokes-Einstein breakdown exponent to better understand the physics behind it. In those studies either different interaction potentials [39] have been used or different spatial

dimensions was used [40–42] to see the change in the exponent. The motivation for going to higher dimensions is that in the mean field limits one expects to have $\omega = 0$. Our study provides an new and easy way to tune this exponent.

To conclude, we have shown by explicitly calculating the distributions of diffusivity for different temperatures for a model glass former in the supercooled regime that the state of the system can be well described by a sparse mixture of “fluid like” regions in the matrix of “solid like” regions on the time scale of α relaxation time. We also showed that the “solid like” regions to a great extent follows the Stokes-Einstein Relation over the whole temperature range. All the deviation comes from the dynamics of the “fluid like” particles leading to a overall breakdown of the relation. Finally we showed how with random pinning one can drastically enhance the decoupling between the translational diffusion and the relaxation time, thereby providing a new and easy way to tune the exponent associated with it to understand the phenomena even better. It will be interesting to extract the length scale associated with this “solid like” and “liquid like” region and compare that with the dynamic heterogeneity length scale and the static length scales [43], work in this direction is in progress and will be published elsewhere.

We want to thank Srikanth Sastry and Chandan Dasgupta for many useful discussions.

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